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Superlegierung auf Nickelbasis mit optimierter Platin-Aluminid Beschichtung

Superalloy à base de nickel ayant un revêtement de platine-aluminure optimisé

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(73) Proprietor: **GENERAL ELECTRIC COMPANY**
Schenectady, NY 12345 (US)

(72) Inventor: **Schaeffer, Jon Conrad**
Miford, Ohio 45150 (US)

(74) Representative: **Pedder, James Cuthbert**
GE London Patent Operation,
Essex House,
12/13 Essex Street
London WC2R 3AA (GB)

(56) References cited:

EP-A- 0 567 755

EP-A- 0 733 723

US-A- 5 077 141

EP-A- 0 587 341

WO-A-95/23243

US-A- 5 427 866

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Description

[0001] This invention relates to nickel-base superalloys used in high-temperature applications, and, more particularly, to articles made of such materials and having an optimized platinum-aluminide protective coating.

[0002] In an aircraft gas turbine (jet) engine, air is drawn into the front of the engine, compressed by a shaft-mounted compressor, and mixed with fuel. The mixture is combusted, and the resulting hot exhaust gases are passed through a turbine mounted on the same shaft. The flow of gas turns the turbine, which turns the shaft and provides power to the compressor. The hot exhaust gases flow from the back of the engine, driving it and the aircraft forwardly.

[0003] The hotter the exhaust gases, the more efficient is the operation of the jet engine. There is thus an incentive to raise the exhaust gas temperature. However, the maximum temperature of the exhaust gases is normally limited by the materials used to fabricate the turbine vanes and turbine blades of the turbine. In current engines, the turbine vanes and blades are made of nickel-based superalloys and can operate at temperatures of up to 1038-1149°C (1900-2100°F).

[0004] Many approaches have been used to increase the operating temperature limit of the turbine blades and vanes. The compositions and processing of the materials themselves have been improved. Physical cooling techniques are used. In one widely used approach, internal cooling channels are provided within the components, and cool air is forced through the channels during engine operation.

[0005] In another approach, a metallic protective coating or a ceramic/metal thermal barrier coating system is applied to the turbine blade or turbine vane component, which acts as a substrate. The metallic protective coating is useful in intermediate-temperature applications. One known type of metallic protective coating is a platinum-aluminide coating that is formed by depositing platinum and aluminum onto the surface of the substrate and then diffusing these constituents into the surface of the substrate.

[0006] The thermal barrier coating system is useful in high-temperature applications. The thermal barrier coating system includes a ceramic thermal barrier coating that insulates the component from the hot exhaust gas, permitting the exhaust gas to be hotter than would otherwise be possible with the particular material and fabrication process of the component. Ceramic thermal barrier coatings usually do not adhere well directly to the superalloys used in the substrates. Therefore, an additional metallic layer called a bond coat is placed between the substrate and the thermal barrier coating. The bond coat is usually made of a nickel-containing overlay alloy, such as a NiCrAlY or a NiCoCrAlY, of a composition more resistant to environmental damage than the substrate. The bond coat may also be made of a diffusional nickel aluminide or platinum aluminide, whose

surface oxidizes to a protective aluminum oxide scale.

[0007] While superalloys coated with such metallic protective coatings or ceramic/metal thermal barrier coating systems do provide substantially improved performance over uncoated materials, there remains room for improvement in elevated temperature performance and environmental resistance. There is an ongoing need for improved metallic protective coatings and bond coats to protect nickel-base superalloys in elevated-temperature applications. This need has become more acute with the development of the newest generation of nickel-base superalloys, inasmuch as the older protective coatings are often not satisfactory with these materials. The present invention fulfills this need, and further provides related advantages.

[0008] EP-A-733723 (constituting prior art under Article 54(3) EPC) discloses a Ni- or Co-based superalloy substrate with average concentration of 8 to 35 percent by weight of platinum and 18 to 28 percent by weight of aluminum deposited thereon.

[0009] WO 95/23243 discloses a platinum aluminum coating whereby the platinum is diffused into a nickel-base substrate before the diffusion of aluminum and silicon. No compositions for the coating are given.

[0010] The present invention provides a metallic overcoating for nickel-base superalloys. The overcoating is a platinum-aluminide useful as a metallic protective coating or as a bond coat for the thermal barrier coating system. The overcoating is in the form of a surface region that is well bonded to the substrate. The platinum-aluminide coating has good elevated-temperature stability and resistance to environmental degradation in typical gas-turbine engine applications.

[0011] In accordance with a first aspect of the invention, there is provided an article having a platinum-aluminide surface region, comprising a substrate having a nickel-base substrate bulk composition and a substrate surface; and a platinum-aluminide surface region at the substrate surface formed by depositing a layer of platinum upon the substrate surface and diffusing the platinum layer into the substrate surface and thereafter providing a source of aluminum and diffusing aluminum into the substrate surface, the surface region having an integrated aluminum content of from 18 to 24 percent by weight and an integrated platinum content of from 18 to 45 percent by weight, balance components of the substrate bulk composition, totalling 100 percent by weight, and wherein both the platinum and aluminum contents are relatively high adjacent to the substrate surface and decrease with increasing distance into the substrate from the substrate surface. Preferably, the surface region has an integrated aluminum content of from 21 to 23 percent by weight and an integrated platinum content of from 30 to 45 percent by weight. All compositions stated herein for surface regions are determined by an integration technique to be discussed subsequently, which effectively determines an averaged composition throughout the surface region. Optionally, a ceramic lay-

er overlies the surface region, to produce a thermal barrier coating system.

[0012] In accordance with a second aspect of the invention, there is provided a method for preparing an article having a platinum-aluminide surface region, comprising the steps of providing a substrate having a nickel-base alloy substrate bulk composition and a substrate surface; thereafter depositing a layer of platinum upon the substrate surface; thereafter diffusing platinum from the layer of platinum into the substrate surface; thereafter providing a source of aluminium; and thereafter diffusing aluminium from the source of aluminium into the substrate surface for a time sufficient to produce a surface region at the substrate surface, the surface region having an integrated aluminium content of from 18 to 24 percent by weight and an integrated platinum content of from 18 to 45 percent by weight, balance components of the substrate bulk composition. Optionally, the substrate and surface region may be annealed, and/or a ceramic layer may be deposited overlying the surface region.

[0013] Platinum-aluminide protective surface regions have been known previously, but the present approach provides an optimized platinum-aluminide coating whose elevated-temperature performance and environmental resistance are improved as compared with prior platinum-aluminide coatings. Moreover, the platinum-aluminide coating of the invention can be utilized with advanced nickel-base superalloys without excessive coating growth during service, surface roughening, production of undesirable phases during service, or reduced stress rupture capabilities.

[0014] The invention will now be described in greater detail, by way of example, with reference to the drawings in which:

Figure 1 is a perspective view of a gas turbine component;

Figure 2A is a schematic sectional view through the component of Figure 1 along line 2-2, showing one embodiment of the invention;

Figure 2B is a schematic sectional view through the component of Figure 1 along line 2-2, showing a second embodiment of the invention;

Figure 3 is a block flow diagram for a method for applying a protective coating to a substrate; and

Figure 4 is a graph illustrating coating performance as a function of composition of the coating.

[0015] Figure 1 depicts a component of a gas turbine engine such as a turbine blade or turbine vane, in this case depicted as a turbine blade 20. The turbine blade 20 includes an airfoil 22 against which the flow of hot exhaust gas is directed. The turbine blade 20 is mounted to a turbine disk (not shown) by a dovetail 24 which extends downwardly from the airfoil 22 and engages a slot on the turbine disk. A platform 26 extends longitudinally outwardly from the area where the airfoil 22 is joined to

the dovetail 24. A number of cooling channels optionally extend through the interior of the airfoil 22, ending in openings 28 in the surface of the airfoil 22. A flow of cooling air is directed through the cooling channels, to reduce the temperature of the airfoil 22.

[0016] The airfoil 22 of the turbine blade 20 is protected by a protective coating 30, two embodiments of which are illustrated in Figure 2A and Figure 2B. In each case, the protective coating 30 is present at a surface 31 of the turbine blade 20, which serves as a substrate 32 for the protective coating 30.

[0017] In the embodiment of Figure 2A, the protective coating 30 comprises a platinum-aluminide region 34 located at the surface 31 of the substrate 32. In the embodiment of Figure 2B, the protective coating 30 comprises a platinum-aluminide region 36 at the surface 31 of the substrate 32 and a ceramic thermal barrier layer 38 overlying the platinum-aluminide region 36. The protective coating 30 shown in Figure 2B, including the metallic region 36 (in this context termed a bond coat) and the ceramic layer 38, is sometimes termed a thermal barrier coating system. The two platinum-aluminide regions 34 and 36 may be of the same or different structures and compositions, within the scope of the invention. The platinum-aluminide regions 34 and 36 are preferably from 0.038 mm (0.0015 inches) to 0.102 mm (0.004 inches) thick, most preferably 0.0635 mm (0.0025 inches) thick.

[0018] Figure 3 is a block flow diagram for a preferred method of preparing the protective coatings of figures 2A and 2B. In a first step, 50, the substrate 32 itself is provided. The substrate is a nickel-base superalloy, preferably an advanced second or third generation, nickel-base single-crystal superalloy containing substantial amounts of both aluminum and rhenium. The substrate is substantially single crystal in form, although small amounts of polycrystalline material are tolerated. The aluminium content is from 5 to 16 weight percent, most preferably 6-7 weight percent, in such advanced superalloys. At least 5 weight percent aluminum is present in order to produce a sufficiently high volume fraction of the strengthening γ' phase. The rhenium content is from 1 to 8 weight percent, most preferably from 2.5 to 6 weight percent, in such advanced superalloys. A most preferred substrate is a single-crystal substrate made of alloy RN5, having a composition, in weight percent, of 7.5 percent cobalt, 7 percent chromium, 6.2 percent aluminum, 6.5 percent tantalum, 5 percent tungsten, 1.5 percent molybdenum, 3 percent rhenium; balance nickel. Optionally, some yttrium and/or hafnium may be present. The approach of the invention is also operable with other advanced alloy substrates such as alloy RN6, having a composition, in weight percent, of 12.5 percent cobalt, 4.5 percent chromium, 6 percent aluminum, 7.5 percent tantalum, 5.8 percent tungsten, 1.1 percent molybdenum, 5.4 percent rhenium, 0.15 percent hafnium, balance nickel; and alloy R142, having a composition, in weight percent, of 12 percent cobalt,

6.8 percent chromium, 6.2 percent aluminum, 6.4 percent tantalum, 4.9 percent tungsten, 1.5 percent molybdenum, 2.8 percent rhenium, 1.5 percent hafnium, balance nickel.

[0019] The optimized platinum-aluminide coating of the invention exhibits excellent performance on a wide variety of substrate materials, but this improved performance is particularly important for these advanced single-crystal nickel-base alloy substrates. These advanced single crystal alloy substrates have higher aluminum contents than prior nickel-base superalloys, resulting in a larger amount of γ phase, about 60-70 volume percent, than prior nickel-base superalloys. They are used at higher operating temperatures, over 1093.3°C (2000°F), than prior nickel-base superalloy substrates, and diffusional effects are accordingly more important. The platinum-aluminide coating of the invention does not experience excessive coating growth, surface roughening, production of undesirable phases during service, or reduced stress rupture capabilities during service at such high temperatures. Accordingly, the combination of such an advanced single-crystal, nickel-base alloy substrate and the platinum-aluminide coating described next is the most preferred embodiment of the invention. The platinum-aluminide coating is not limited to use on such advanced single-crystal superalloys, however.

[0020] A layer of platinum is deposited on the surface of the substrate 32 as it then is presented, numeral 52. The layer of platinum is preferably deposited by electroplating, but other operable techniques such as sputtering and metallo-organic chemical vapor deposition may also be used. The layer of platinum is desirably 0.0076 mm (0.0003 inches) thick.

[0021] Platinum from the layer of platinum is diffused into the surface of the substrate by heating the substrate and the deposited layer of platinum, numeral 54. The preferred diffusion treatment is 2 hours at 982-1093.3°C (1800-2000°F). The steps 52 and 54 may be conducted simultaneously or serially.

[0022] A source of aluminum is provided, numeral 56, by any operable technique. Preferably, a hydrogen and a halide gas is contacted with aluminum metal or an aluminum alloy to form the corresponding aluminum halide gas. The aluminum halide gas is contacted to the previously deposited platinum layer overlying the substrate, depositing an aluminum layer over the platinum substrate. The reactions occur at elevated temperature so that aluminum atoms transferred to the surface diffuse into the surface of the platinum-enriched region and the substrate, numeral 58. The steps 56 and 58 are therefore typically conducted simultaneously.

[0023] The temperature of the treatment, the source composition, the exposure time, and the quantity of aluminum-source gas determine the amount of aluminum transferred to the substrate and diffused into the substrate. The activity of the aluminum is determined with a pure nickel foil 0.025 millimeters thick that is placed in

the aluminizing reactor at the same locations where substrates are to be placed. Complications associated with the measurement of aluminum in multicomponent systems are thereby avoided. The foil is processed in the reactor so that the foil saturates with aluminum. The aluminum content of the foil is measured by acid digestion and analysis with a suitable method such as inductively coupled plasma emission spectroscopy. From these measurements, the processing of the aluminizing treatment was determined. The preferred processing produces an activity of between 40 and 50 atomic percent in a pure nickel foil. In a preferred approach, the aluminizing and diffusion treatment is accomplished at a temperature of 1051.7-1121°C (1925-2050°F) for 4-16 hours.

[0024] After the diffusion treatment is complete, the chemical compositions of the platinum-aluminide region 34, 36 and the portion of the substrate 32 immediately adjacent to the platinum-aluminum region 34, 36 vary as a function of depth below the surface. The aluminum content and the platinum content of the platinum-aluminum region 34, 36 are relatively high adjacent to the surface 31, and decrease with increasing depth into the region 34, 36 and the substrate 32. The remainder of the composition, totalling 100 weight percent, is formed of components of the bulk composition of the substrate alloy, which is high at a large depth below the surface 31 and decreases to a lower value immediately adjacent to the surface 31.

[0025] Because of this variation of composition with depth, the compositions of surface regions are measured by an integration method. The coated substrate is sectioned perpendicular to the surface. The weight percent of aluminum, platinum, and other elements of interest as a function of distance from the surface is determined by any technique that provides local compositions, such as an electron microprobe with a wavelength dispersive spectrometer or energy dispersive spectrometer (in conjunction with appropriate calibration standards). Measurements are taken with an electron raster that produces at least a 5 micrometer by 5 micrometer window. Such compositional measurement techniques are known in the art. Compositional measurements are taken at locations starting within 2-3 micrometers of the outer exposed surface, and increasing depth increments of 5 micrometers or less from the prior measurement. The weight percent content of the element of interest is plotted as a function of distance from the outer exposed surface, up to a maximum distance that serves as the upper limit of integration. The upper limit of the integration is selected as the distance where the weight percent of aluminum has decreased to 18 percent from the higher values closer to the surface, because below 18 percent aluminum the β -NiAl is not stable. The area under the curve is determined by any appropriate technique such as a trapezoidal approximation, and divided by the value of the upper limit of integration.

[0026] Extensive testing, to be described in greater

detail subsequently, was undertaken to determine the characteristics, properties, and processing of the optimum platinum-aluminum region 34, 36. The result is that the region 34, 36 has an integrated composition of from 18 to 24 weight percent aluminum and from 18 to 45 weight percent platinum. More preferably, the integrated composition is from 21 to 23 weight percent aluminum and from 30 to 45 weight percent platinum. The balance of the composition is interdiffused components of the substrate, principally nickel, cobalt, and chromium, so that the total of aluminum, platinum, and the diffused components composition is 100 percent.

[0027] This region 34, 36 is a single-phase, relatively ductile composition of aluminum, platinum, nickel, and the diffused components of the substrate. In the preferred approach, the region 34, 36 is 0.0635mm (0.0025 inches) thick.

[0028] The process of Figure 3 described to this point may optionally be followed by either or both of two additional processing steps. The substrate 32 and interdiffused region 34, 36 may be annealed to stress relieve the interdiffused region 34, 36, numeral 60. This annealing procedure, while widely used for some protective coatings, has not been found necessary with the present approach. If it is used, a preferred annealing treatment is a temperature of 982-1043.3°C (1800-2000°F) for a time of 1/4 to 2 hours.

[0029] A ceramic layer may optionally be deposited over the surface 31 of the substrate 30, numeral 62, if the final structure is to be a thermal barrier coating system of the type depicted in Figure 2B. The ceramic layer for a thermal barrier coating 38 is preferably yttria-stabilized zirconia (YSZ) having a composition zirconia and about 6-8 percent by weight yttria, and 0.127-0.381 mm (0.005-0.015 inches) thick. The YSZ is deposited by any operable technique, most preferably electron beam physical vapor deposition.

[0030] Coatings of a variety of platinum-aluminum region compositions were prepared by the preferred approach described above using RNS substrates. The coated specimens were tested in burner rigs in a high-velocity 0.5 ppm salt environment at 1178°C (2150°F). The lives of the coated specimens were determined in hours of exposure per 0.1254 mm (mil (0.001 inch)) of coating. Figure 4 depicts the results of these tests. There is a distinct region of significantly improved performance, for platinum-aluminum regions having an integrated aluminum content of from 18 to 24 percent by weight and an integrated platinum content of from 18 to 45 percent by weight, balance components of the substrate bulk composition. Particularly desirable results are obtained for an optimum compositional range wherein the integrated aluminum content of the surface region is from 21 to 23 percent by weight and the integrated platinum content of the surface region is from 30 to 45 percent by weight. Outside of these limits, the protection afforded by the surface region decreases.

[0031] This invention has been described in connec-

tion with specific embodiments and examples. However, those skilled in the art will recognize various modifications and variations of which the present invention is capable without departing from its scope as represented by the appended claims.

Claims

1. An article having a platinum-aluminide surface region, comprising:

a substrate having a nickel-base substrate bulk composition and a substrate surface; and
a platinum-aluminide surface region at the substrate surface formed by depositing a layer of platinum upon the substrate surface and diffusing the platinum layer into the substrate surface and thereafter providing a source of aluminum and diffusing aluminum into the substrate surface, the surface region having an integrated aluminum content of from 18 to 24 percent by weight and an integrated platinum content of from 18 to 45 percent by weight, balance components of the substrate bulk composition, totalling 100 percent by weight, and wherein both the platinum and aluminium contents are relatively high adjacent to the substrate surface and decrease with increasing distance into the substrate from the substrate surface.

2. The article of claim 1, wherein the integrated aluminium content of the surface region is from 21 to 23 percent by weight and the integrated platinum content of the surface region is from 30 to 45 percent by weight.

3. The article of claim 1 or 2, wherein the article further includes a ceramic layer overlying the surface region, the ceramic layer having a thickness of from 0.127 mm (0.005 inches) to 0.381 mm (0.015 inches).

4. The article of any preceding claim, wherein the article is a turbine blade or a turbine vane.

5. The article of any preceding claim, wherein the nickel-base alloy substrate is substantially a single crystal and the substrate bulk composition includes from 6 to 41 weight percent aluminium and from 1 to 8 weight percent rhenium.

6. The article of any one of claims 1 to 4, wherein the nickel-base alloy substrate is substantially a single crystal and the substrate bulk composition is selected from the group consisting of (a) 7.5 percent cobalt, 7 percent chromium, 6.2 percent aluminium, 6.5 percent tantalum, 5 percent tungsten, 1.5 per-

cent molybdenum, 9 percent rhenium, balance nickel; (b) 12.5 percent cobalt, 4.5 percent chromium, 6 percent aluminium, 7.5 percent tantalum, 5.8 percent tungsten, 1.1 percent molybdenum, 5.4 percent rhenium, 0.15 percent hafnium, balance nickel; and (c) 12 percent cobalt, 6.8 percent chromium, 6.2 percent aluminium, 6.4 percent tantalum, 4.9 percent tungsten, 1.5 percent molybdenum, 2.8 percent rhenium, 1.5 percent hafnium, balance nickel.

7. A method for preparing an article having a platinum-aluminide surface region, comprising the steps of:

providing a substrate having a nickel-base alloy substrate bulk composition and a substrate surface; thereafter depositing a layer of platinum upon the substrate surface; thereafter diffusing platinum from the layer of platinum into the substrate surface; thereafter providing a source of aluminium; and thereafter diffusing aluminium from the source of aluminium into the substrate surface for a time sufficient to produce a surface region at the substrate surface, the surface region having an integrated aluminium content of from 18 to 24 percent by weight and an integrated platinum content of from 18 to 45 percent by weight, balance components of the substrate bulk composition.

8. The method of claim 7, wherein the step of diffusing aluminium includes the step of heating the substrate surface and source of aluminium to a temperature of 1051.7-1121°C (1925 - 2050°F) for a time of from 4 to 16 hours.
9. The method of claim 7 or 8, wherein the step of providing a source of aluminium includes the step of providing a source of aluminium in contact with the substrate surface, the source having an activity of 40 to 50 atomic percent as measured in a pure nickel foil.
10. The method of claim 7, 8 or 9, wherein the step of diffusing platinum includes the step of heating the substrate and layer of platinum to a temperature of 982-1093.3°C (1800 - 2000°F) for a time of 2 hours.
11. The method of any one of claims 7 to 10, including an additional step, after the step of diffusing aluminium, of depositing a ceramic layer overlying the substrate surface.
12. The method of any one of claims 7 to 11, wherein

the step of diffusing aluminium includes the step of diffusing aluminium from the source of aluminium into the substrate surface for a time sufficient that the surface region has an integrated aluminium content of from 21 to 23 percent by weight and an integrated platinum content of from 30 to 45 percent by weight, balance components of the substrate bulk composition.

13. The method of any one of claims 7 to 12, wherein the step of providing a substrate includes the step of providing a nickel-base alloy substrate which is substantially a single crystal and has a composition that includes from 6 to 41 weight percent aluminium and from 1 to 8 weight percent rhenium.
14. The method of any one of claims 7 to 12, wherein the step of providing a substrate includes the step of providing a nickel-base alloy substrate which is substantially a single crystal and has a composition selected from the group consisting of (a) 7.5 percent cobalt, 7 percent chromium, 6.2 percent aluminium, 6.5 percent tantalum, 5 percent tungsten, 1.5 percent molybdenum, 3 percent rhenium, balance nickel; (b) 12.5 percent cobalt, 4.5 percent chromium, 6 percent aluminium, 7.5 percent tantalum, 5.8 percent tungsten, 1.1 percent molybdenum, 5.4 percent rhenium, 0.15 percent hafnium, balance nickel; and (c) 12 percent cobalt, 6.8 percent chromium, 6.2 percent aluminium, 6.4 percent tantalum, 4.9 percent tungsten, 1.5 percent molybdenum, 2.8 percent rhenium, 1.5 percent hafnium, balance nickel.

Patentansprüche

1. Gegenstand mit einem Platinaluminid-Oberflächenbereich, umfassend:
- ein Substrat mit einer Massenzusammensetzung auf Nickelbasis und einer Substratoberfläche und einem Platinaluminid-Oberflächenbereich an der Substratoberfläche, gebildet durch Abscheiden einer Platinschicht auf der Substratoberfläche und Diffundieren der Platinschicht in die Substratoberfläche und danach Bereitstellen einer Aluminiumquelle und Diffundieren von Aluminium in die Substratoberfläche, wobei der Substratbereich einen integrierten Aluminiumgehalt von 18 bis 24 Gew.-% und einen integrierten Platingehalt von 18 bis 45 Gew.-%, Rest Komponenten der Substrat-Massenzusammensetzung, aufweist, die insgesamt 100 Gew.-% ergeben, und worin die Platin- und Aluminiumgehalte relativ hoch benachbart der Substratoberfläche sind und mit zunehmender

dem Abstand von der Substratoberfläche in das Substrat hinein abnehmen.

2. Gegenstand nach Anspruch 1, worin der integrierte Aluminiumgehalt des Oberflächenbereiches von 21 bis 23 Gew.-% und der integrierte Platingehalt des Oberflächenbereiches von 30 bis 45 Gew.-% beträgt.
3. Gegenstand nach Anspruch 1 oder 2, worin der Gegenstand weiter eine Keramikschicht aufweist, die auf dem Oberflächenbereich liegt, wobei die Keramikschicht eine Dicke von 0,127 mm (0,005 inches) bis 0,381 mm (0,015 inches) aufweist.
4. Gegenstand nach einem vorhergehenden Anspruch, wobei der Gegenstand eine Turbinen-Laufschaukel oder eine Turbinen-Leitschaukel ist.
5. Gegenstand nach einem vorhergehenden Anspruch, worin das Substrat auf der Grundlage einer Nickelbasislegierung im Wesentlichen einkristallin ist und die Substrat-Massenzusammensetzung von 6 bis 41 Gew.-% Aluminium und von 1 bis 8 Gew.-% Rhenium einschließt.
6. Gegenstand nach einem der Ansprüche 1 bis 4, worin das Nickelbasis-Legierungssubstrat im Wesentlichen einkristallin ist und die Substrat-Massenzusammensetzung ausgewählt ist aus der Gruppe bestehend aus (a) 7,5% Cobalt, 7% Chrom, 6,2% Aluminium, 6,5% Tantal, 5% Wolfram, 1,5% Molybdän, 3% Rhenium, Rest Nickel; (b) 12,5% Cobalt, 4,5% Chrom, 6% Aluminium, 7,5% Tantal, 5,8% Wolfram, 1,1% Molybdän, 5,4% Rhenium, 0,15% Hafnium, Rest Nickel und (c) 12% Cobalt, 6,8% Chrom, 6,2% Aluminium, 6,4% Tantal, 4,9% Wolfram, 1,5% Molybdän, 2,8% Rhenium, 1,5% Hafnium, Rest Nickel.
7. Verfahren zum Herstellen eines Gegenstandes mit einem Platin-aluminid-Oberflächenbereich, umfassend die Stufen:

Schaffen eines Substrates mit einer Massenzusammensetzung aus einer Legierung auf Nickelbasis und einer Substratoberfläche, danach Abscheiden einer Platinschicht auf der Substratoberfläche, danach Diffundieren von Platin aus der Platinschicht in die Substratoberfläche, danach Schaffen einer Aluminiumquelle und danach Diffundieren von Aluminium aus der Aluminiumquelle in die Substratoberfläche für eine genügende Zeit, um einen Oberflächenbereich an der Substratoberfläche zu erzeugen, wobei der Substratbereich einen integrierten Aluminiumgehalt von 18 bis 24 Gew.-% und einen inte-

grierten Platingehalt von 18 bis 45 Gew.-%, Rest Komponenten der Substrat-Massenzusammensetzung, aufweist.

8. Verfahren nach Anspruch 7, worin die Stufe des Diffundierens von Aluminium die Stufe des Erhitzens der Substratoberfläche und der Aluminiumquelle auf eine Temperatur von 1051,7-1121°C (1925-2050°F) für eine Dauer von 4 bis 16 Stunden einschließt.
9. Verfahren nach Anspruch 7 oder 8, worin die Stufe des Schaffens einer Aluminiumquelle die Stufe des Schaffens einer Aluminiumquelle in Kontakt mit der Substratoberfläche einschließt, wobei die Quelle eine Aktivität von 40 bis 50 Atom-%, gemessen in einer reinen Nickelfolie, aufweist.
10. Verfahren nach Anspruch 7, 8 oder 9, worin die Stufe des Diffundierens von Platin die Stufe des Erhitzens des Substrates und der Platinschicht auf eine Temperatur von 982-1093,3°C (1800-2000°F) für eine Zeit von 2 Stunden einschließt.
11. Verfahren nach einem der Ansprüche 7 bis 10, das nach der Stufe des Diffundierens von Aluminium eine zusätzliche Stufe des Abscheidens einer Keramikschicht einschließt, die über der Substratoberfläche liegt.
12. Verfahren nach einem der Ansprüche 7 bis 11, worin die Stufe des Diffundierens von Aluminium die Stufe des Diffundierens von Aluminium aus der Aluminiumquelle in die Substratoberfläche für eine genügende Zeit einschließt, so dass der Oberflächenbereich einen integrierten Aluminiumgehalt von 21 bis 23 Gew.-% und einen integrierten Platingehalt von 30 bis 45 Gew.-%, Rest Komponenten der Substrat-Massenzusammensetzung, aufweist.
13. Verfahren nach einem der Ansprüche 7 bis 12, worin die Stufe des Schaffens eines Substrates die Stufe der Schaffung eines Substrates aus einer Nickelbasislegierung einschließt, das im Wesentlichen einkristallin ist und eine Zusammensetzung aufweist, die von 6 bis 41 Gew.-% Aluminium und von 1 bis 8 Gew.-% Rhenium enthält.
14. Verfahren nach einem der Ansprüche 7 bis 12, worin die Stufe der Schaffung eines Substrates die Stufe der Schaffung eines Nickelbasis-Legierungssubstrates einschließt, das im Wesentlichen einkristallin ist und eine Zusammensetzung aufweist, ausgewählt aus der Gruppe bestehend aus (a) 7,5% Cobalt, 7% Chrom, 6,2% Aluminium, 6,5% Tantal, 5% Wolfram, 1,5% Molybdän, 3% Rhenium, Rest Nickel; (b) 12,5% Cobalt, 4,5% Chrom, 6% Aluminium, 7,5% Tantal, 5,8% Wolfram, 1,1% Molybdän, 5,4%

Rhénium, 0,15% Hafnium, Rest Nickel und (c) 12% Cobalt, 6,8% Chrome, 6,2% Aluminium, 6,4% Tantale, 4,9% Wolfram, 1,5% Molybdène, 2,8% Rhénium, 1,5% Hafnium, Rest Nickel.

Revendications

1. Pièce présentant une zone superficielle de platine-aluminure, qui comprend :

un élément de base ayant la composition globale d'un support en alliage à base de nickel et présentant une surface, et une zone superficielle de platine-aluminure, située à la surface de l'élément de base, que l'on forme en déposant une couche de platine sur la surface de l'élément de base et en faisant diffuser la couche de platine à travers la surface de l'élément de base, puis en fournissant une source d'aluminium et en faisant diffuser de l'aluminium à travers la surface de l'élément de base, la zone superficielle ayant une teneur en aluminium, déterminée par intégration, de 18 à 24 pour-cent en poids et une teneur en platine, déterminée par intégration, de 18 à 45 pour-cent en poids, le complément à 100 pour-cent en poids étant formé par des constituants de la composition globale de l'élément de base, et la teneur en platine et la teneur en aluminium étant toutes les deux relativement élevées au voisinage immédiat de la surface de l'élément de base et diminuant lorsque la distance dans l'élément de base à partir de la surface de l'élément de base augmente.

2. Pièce selon la revendication 1, pour laquelle la teneur en aluminium, déterminée par intégration, de la zone superficielle est de 21 à 23 pour-cent en poids et la teneur en platine, déterminée par intégration, de la zone superficielle est de 30 à 45 pour-cent en poids.
3. Pièce selon la revendication 1 ou 2, qui comporte en outre une couche de céramique recouvrant la zone superficielle, cette couche de céramique ayant une épaisseur de 0,127 mm (0,005 pouce) à 0,381 mm (0,015 pouce).
4. Pièce selon l'une quelconque des revendications précédentes, qui est une pale de turbine ou une aube de turbine.
5. Pièce selon l'une quelconque des revendications précédentes, pour laquelle l'élément de base en alliage à base de nickel est pratiquement un monocristal et la composition globale de l'élément de base contient 6 à 41 pour-cent en poids d'aluminium

et 1 à 8 pour-cent en poids de rhénium.

6. Pièce selon l'une quelconque des revendications 1 à 4, pour laquelle l'élément de base en alliage à base de nickel est pratiquement un monocristal et la composition globale de l'élément de base est choisie parmi les suivantes :

(a) 7,5 pour-cent de cobalt, 7 pour-cent de chrome, 6,2 pour-cent d'aluminium, 6,5 pour-cent de tantale, 5 pour-cent de tungstène, 1,5 pour-cent de molybdène, 3 pour-cent de rhénium, complément constitué de nickel; (b) 12,5 pour-cent de cobalt, 4,5 pour-cent de chrome, 6 pour-cent d'aluminium, 7,5 pour-cent de tantale, 5,8 pour-cent de tungstène, 1,1 pour-cent de molybdène, 5,4 pour-cent de rhénium, 0,15 pour-cent de hafnium, complément constitué de nickel; et (c) 12 pour-cent de cobalt, 6,8 pour-cent de chrome, 6,2 pour-cent d'aluminium, 6,4 pour-cent de tantale, 4,9 pour-cent de tungstène, 1,5 pour-cent de molybdène, 2,8 pour-cent de rhénium, 1,5 pour-cent de hafnium, complément constitué de nickel.

7. Procédé de préparation d'une pièce présentant une zone superficielle de platine-aluminure, qui comprend les étapes consistant à :

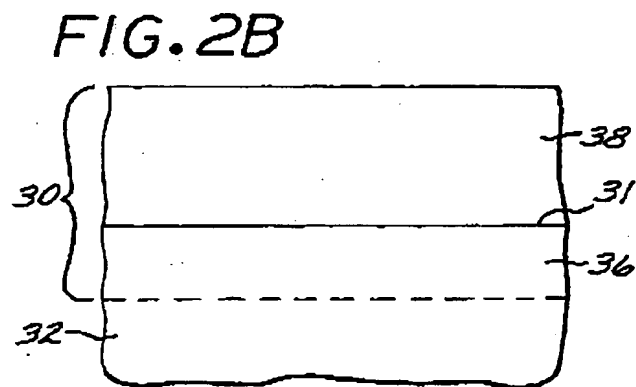
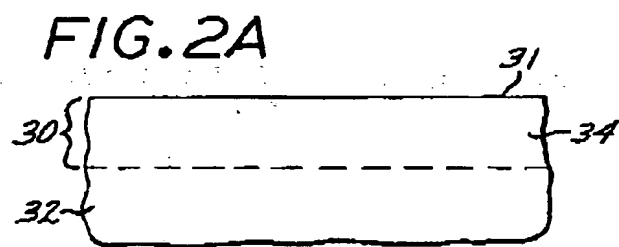
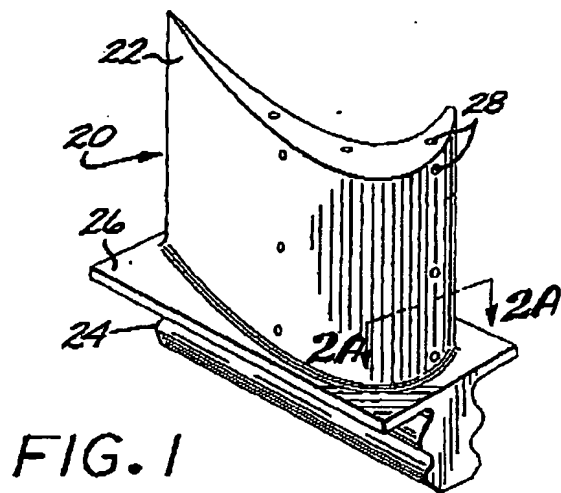
fournir un élément de base ayant la composition globale d'un support en alliage à base de nickel et présentant une surface, déposer ensuite une couche de platine sur la surface de l'élément de base, faire diffuser ensuite le platine à partir de la couche de platine à travers la surface de l'élément de base, fournir ensuite une source d'aluminium, et faire diffuser ensuite de l'aluminium provenant de la source d'aluminium à travers la surface de l'élément de base pendant un temps suffisant pour former une zone superficielle à la surface de l'élément de base, la zone superficielle ayant une teneur en aluminium, déterminée par intégration, de 18 à 24 pour-cent en poids et une teneur en platine, déterminée par intégration, de 18 à 45 pour-cent en poids, le complément étant formé par des constituants de la composition globale de l'élément de base.

8. Procédé selon la revendication 7, dans lequel l'étape de diffusion de l'aluminium comprend le chauffage de la surface de l'élément de base et de la source d'aluminium à une température de 1051,7 à 1121°C (1925 à 2050°F), pendant une durée de 4 à 16 heures.
9. Procédé selon la revendication 7 ou 8, dans lequel l'étape de fourniture d'une source d'aluminium comprend la mise d'une source d'aluminium en contact

avec la surface de l'élément de base, la source ayant une activité de 40 à 50 pour-cent en atomes, cette activité étant mesurée pour une feuille de nickel pur.

cent de hafnium, complément constitué de nickel.

10. Procédé selon l'une quelconque des revendications 7 à 9, dans lequel l'étape de diffusion du platine comprend le chauffage de l'élément de base et de la couche de platine à une température de 982 à 1093,3°C (1800 à 2000°F), pendant une durée de 2 heures.
11. Procédé selon l'une quelconque des revendications 7 à 10, qui comprend après l'étape de diffusion de l'aluminium, une étape supplémentaire de dépôt d'une couche de céramique recouvrant la surface de l'élément de base.
12. Procédé selon l'une quelconque des revendications 7 à 11, dans lequel l'étape de diffusion de l'aluminium comprend la diffusion de l'aluminium provenant de la source d'aluminium à travers la surface de l'élément de base, pendant un temps suffisant pour que la zone superficielle ait une teneur en aluminium, déterminée par intégration, de 21 à 23 pour-cent en poids et une teneur en platine, déterminée par intégration, de 30 à 45 pour-cent en poids, le complément étant formé par des constituants de la composition globale de l'élément de base.
13. Procédé selon l'une quelconque des revendications 7 à 12, dans lequel l'étape de fourniture d'un élément de base comprend la fourniture d'un élément de base en alliage à base de nickel, qui est pratiquement un monocristal et qui a une composition contenant 6 à 41 pour-cent en poids d'aluminium et 1 à 8 pour-cent en poids de rhénium.
14. Procédé selon l'une quelconque des revendications 7 à 12, dans lequel l'étape de fourniture d'un élément de base comprend la fourniture d'un élément de base en alliage à base de nickel, qui est pratiquement un monocristal et qui a une composition choisie parmi les suivantes : (a) 7,5 pour-cent de cobalt, 7 pour-cent de chrome, 6,2 pour-cent d'aluminium, 6,5 pour-cent de tantale, 5 pour-cent de tungstène, 1,5 pour-cent de molybdène, 3 pour-cent de rhénium, complément constitué de nickel ; (b) 12,5 pour-cent de cobalt, 4,5 pour-cent de chrome, 6 pour-cent d'aluminium, 7,5 pour-cent de tantale, 5,8 pour-cent de tungstène, 1,1 pour-cent de molybdène, 5,4 pour-cent de rhénium, 0,15 pour-cent de hafnium, complément constitué de nickel ; et (c) 12 pour-cent de cobalt, 6,8 pour-cent de chrome, 6,2 pour-cent d'aluminium, 6,4 pour-cent de tantale, 4,9 pour-cent de tungstène, 1,5 pour-cent de molybdène, 2,8 pour-cent de rhénium, 1,5 pour-



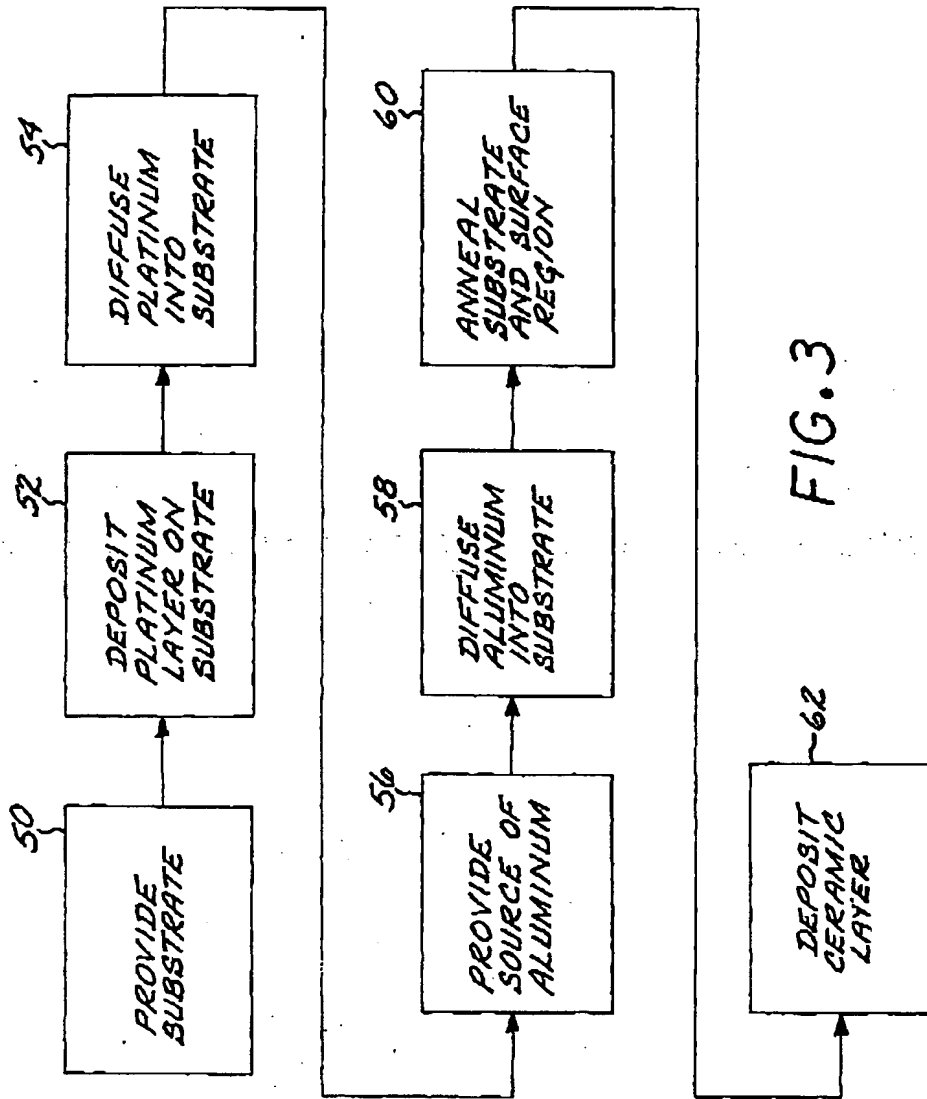


FIG. 3

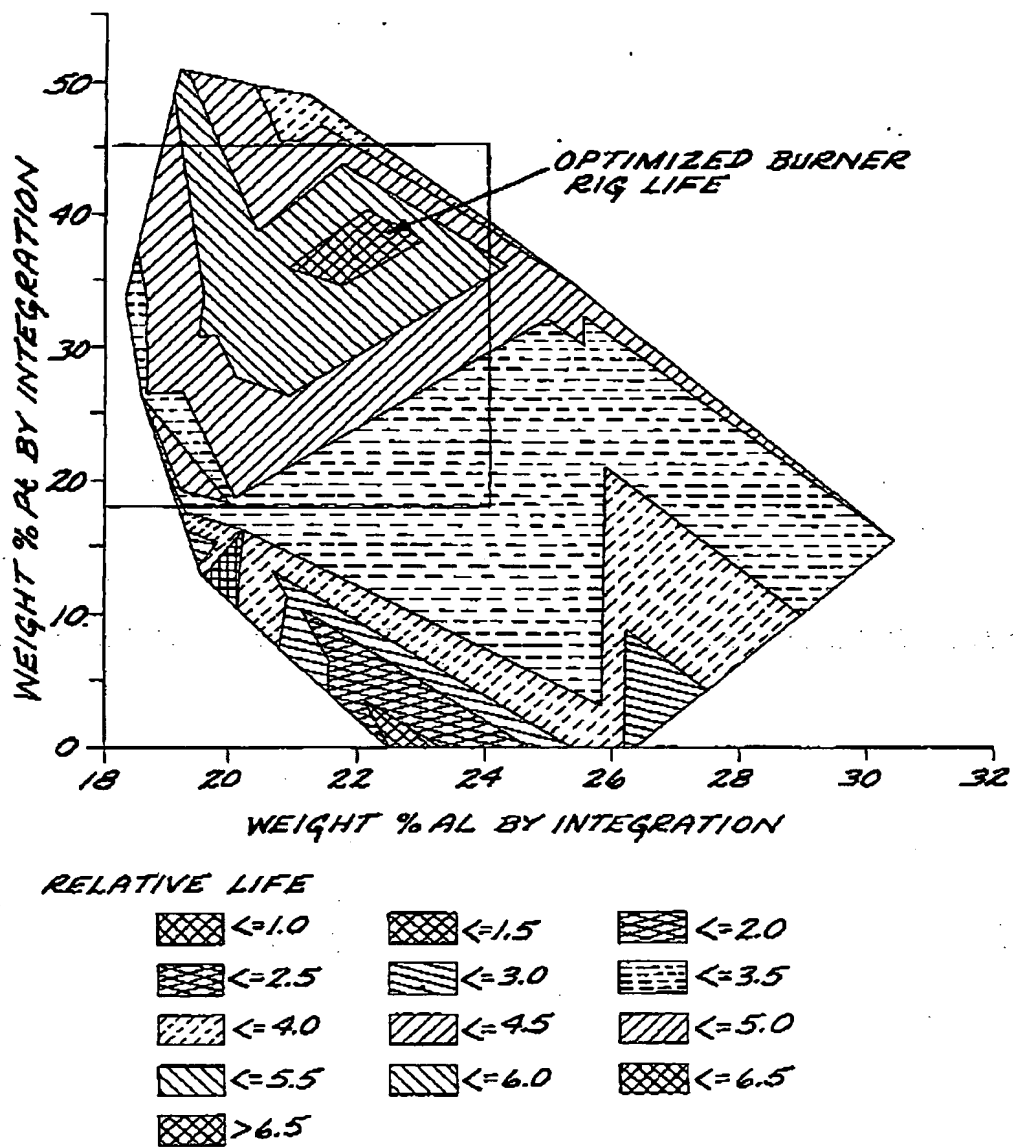


FIG.4

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